



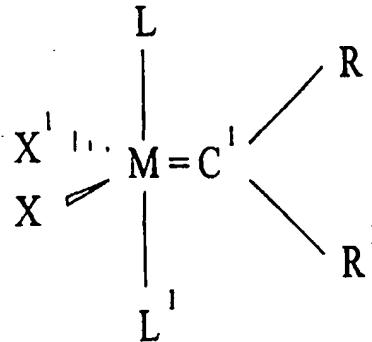
## INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

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(54) Title: CATALYST COMPLEX WITH CARBENE LIGAND

## (57) Abstract

Catalytic complexes including a metal atom having anionic ligands, at least one nucleophilic carbene ligand, and an alkylidene, vinylidene, or allenylidene ligand. The complexes are highly stable to air, moisture and thermal degradation. The complexes are designed to efficiently carry out a variety of olefin metathesis reactions.



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CATALYST COMPLEX WITH CARBENE LIGAND  
Cross Reference To Related Applications

This application claims priority from U.S. Provisional Application Serial Nos. 60/099,722, filed 5 September 10, 1998, and 60/115,358, filed January 8, 1999.

Statement as to Federally Sponsored Research

This invention was made with Government support 10 under Grant No. CHE-963611 awarded by the National Science Foundation. The Government has certain rights in this invention.

Background of the Invention

15 The invention relates to metal carbene complexes. More particularly, it relates to catalyst systems comprising metal carbene complexes.

Catalysts previously known in the art are described in, for example, U.S. Patent No. 5,312,940 to 20 Grubbs et al. These catalysts include bis(phosphine) complexes which involve the use of costly phosphine ( $PR_3$ ) ligands. The stabilities of such systems, as determined by, for example, P-C bond degradation at elevated temperature, are limited. Also, the rates at which 25 bis(phosphine) catalysts carry out particular reactions are limited. Thus, industrial applications involving large-scale syntheses are not as efficient as they could be.

Previously available catalytic systems are also 30 limited in their ability to make highly substituted ring-closing metathesis (RCM) products. Thus, bis(phosphine) catalysts cannot reliably close dienes to make tri-substituted cyclic alkenes, and they fail to make tetra-substituted cyclic alkenes in all but a few cases.

Although Schrock catalysts are available to carry out this type of reaction, such systems are quite sensitive.

Thus there exists in the art a need for a generally air- and moisture-sensitive catalyst system able to carry out RCM reactions efficiently and reliably, and also without excessive thermal sensitivity.

Summary of the Invention

The invention provides catalysts including metal carbene complexes which are useful for synthetic chemical reactions. The catalysts include at least one bulky nucleophilic carbene ligated to the metal center. Methods of making such catalysts, and ligands useful for such catalysts are also provided in the present invention.

The inventive catalytic complexes are thermally stable, have high reaction rates, and are air- and moisture-stable. The catalysts of the invention are easy to synthesize, have high catalytic activity, and are relatively inexpensive, due to the availability of the nucleophilic carbene ligand. The catalysts are useful in the facilitation of chemical reactions, including applications in the pharmaceutical industry, fine chemical synthesis, and the synthesis of polymers.

Unless otherwise defined, all technical and scientific terms used herein have the same meaning as commonly understood by one of ordinary skill in the art to which this invention belongs. Although methods and materials similar or equivalent to those described herein can be used in the practice or testing of the present invention, suitable methods and materials are described below. In case of conflict, the present specification, including definitions, will control. In addition, the materials, methods, and examples are illustrative only and not intended to be limiting.

Other features and advantages of the invention will be apparent from the following detailed description, and from the claims.

5                   Brief Description of the Drawings

Fig. 1A is a general structure of a first particular embodiment of a catalytic complex, having a first ligation pattern.

10                  Fig. 1B is a general structure of a first particular embodiment of a catalytic complex, having a second ligation pattern.

Fig. 1C is a general structure of a first particular embodiment of a catalytic complex, having a third ligation pattern.

15                  Fig. 2A is an example of a nucleophilic carbene ligand which can be utilized in certain embodiments of the present invention.

Fig. 2B is a particular nucleophilic carbene which can be utilized in certain embodiments of the invention.

20                  Fig. 2C is a particular nucleophilic carbene which can be utilized in certain embodiments of the invention.

Fig. 3A is a general structure of a second particular embodiment of a catalytic complex, having a first ligation pattern.

25                  Fig. 3B is a general structure of a second particular embodiment of a catalytic complex, having a second ligation pattern.

Fig. 3C is a general structure of a second particular embodiment of a catalytic complex, having a third ligation pattern.

Fig. 4 is an ORTEP diagram of the crystal structure of  $Cp^*Ru(IMes)Cl$ .

Fig. 5 is an ORTEP diagram of the crystal structure of  $Cp^*Ru(PCy_3)Cl$ .

Fig. 6 is an ORTEP diagram of the crystal structure of  $\text{Cl}_2\text{Ru}(\text{PCy}_3)(\text{IMes})(=\text{CHPh})$ .

Detailed Description

5 The invention includes a catalytic complex for the carrying out of chemical reactions. The complex includes a metal atom and various ligands. A particular embodiment of the catalytic complex is depicted in Figs. 1A, 1B and 1C.

10 Making reference to Fig. 1A, metal atom M can be a transition metal generally having an electron count of from 14 to 18. Particular metals of this description which have been found useful in the present invention include ruthenium and osmium.

15 Ligated to metal atom M are a number of ligands. At least one of these ligands is a carbene ligand, which is functionally an olefin metathesis active fragment, having a carbon atom  $\text{C}^1$  which can be further bonded up to two other groups. The bond from metal atom M to carbon atom  $\text{C}^1$  can be formulated as the double bonded  $\text{M}=\text{C}^1$ , 20 although other canonical forms are evidently involved, as detailed in Cotton and Wilkinson's Advanced Inorganic Chemistry, 5th Edition, John Wiley & Sons, New York (1980), pp 1139-1140.

25 As noted, carbon atom  $\text{C}^1$  can further bonded to up to two other groups, R and  $\text{R}^1$ , and in this case the olefin metathesis active fragment is referred to as an alkylidene. These R and  $\text{R}^1$  groups are independently selected from a large number of atoms and substituents.

30 These include hydrogen, alkyl groups having from 1 to 20 carbon atoms (such as methyl, ethyl, n-propyl, iso-propyl, n-butyl, iso-butyl, sec-butyl, and the like). Also possible as either R or  $\text{R}^1$  are alkenyl or alkynyl substituents having from 2 to 20 carbon atoms. The

35 groups R and  $\text{R}^1$  can also include alkoxy carbonyl

substituents having from 2 to 20 carbons atoms, aryl groups, carboxylate substituents having from 1 to 20 carbon atoms, alkoxy substituents having from 1 to 20 carbon atoms, alkenyloxy or alkynyloxy substituents

5 having from 2 to 20 carbon atoms, as well as aryloxy substituents. Also included are alkylthio, alkylsulfonyl, and alkylsulfinyl substituents with from 1 to 20 carbon atoms. Each of the above classes of R or R<sup>1</sup> substituent can be further optionally substituted with halogen, or 10 with alkyl or alkoxy groups of from 1 to 10 carbon atoms, or aryl groups. Further substitution of R and R<sup>1</sup> can include the functional groups of hydroxyl, thiol, thioether, ketone, aldehyde, ester, amide, amine, imine, nitro, carboxylic acid, disulfide, carbonate, isocyanate, 15 carbodiimide, carboalkoxy, carbamate, and halogen.

Any of the above R or R<sup>1</sup> substituents can include various structural isomers (n-, iso-, sec-, and tert-), cyclic or polycyclic isomers, and multiply unsaturated variants.

20 Particularly useful R and R<sup>1</sup> substituents are vinyl, phenyl, hydrogen, wherein the vinyl and phenyl substituents are optionally substituted with one or more moieties selected from C<sub>1</sub>-C<sub>5</sub> alkyl, C<sub>1</sub>-C<sub>5</sub> alkoxy, phenyl or a functional group, such as chloride, bromide, iodide, 25 fluoride, nitro, or dimethylamine.

When carbon atom C<sup>1</sup> is not directly bonded to two groups R and R<sup>1</sup>, it is further bonded to another carbon C<sup>2</sup>, which is in turn bonded to previously described substituents R and R<sup>1</sup>, and the olefin metathesis active 30 carbene ligand is referred to as a vinylidene. This is shown in Fig. 1B. This ligation is generally achieved by means of a double bond from C<sup>1</sup> to C<sup>2</sup>.

Also, as shown in Fig. 1C, C<sup>2</sup> can be further bonded to another carbon C<sup>3</sup>. This type of olefin 35 metathesis active carbene ligand is referred to as an

allenylidene.  $C^3$  is further bonded to the above-described substituents  $R$  and  $R^1$ . Carbons  $C^1$ ,  $C^2$  and  $C^3$  are each  $sp^2$  hybridized carbons, and the absence of one or two of such carbons in the allenylidene structure of Fig. 1C gives 5 the respective vinylidene or alkylidene or Fig. 1B or 1A, respectively.

It has been found that when  $R$  or  $R^1$  are aryl, the allenylidene ligand can undergo a rearrangement, forming a different structure in which a ring is formed between  $C^1$  10 and an aryl carbon of  $R$  or  $R^1$ . For example, if  $C^1=C^2=C^3Ph_2$  is ligated to metal  $M$  in the systems described herein, the olefin metathesis active carbene ligand is not an allenylidene, but rather a cyclized vinyl carbene, an "indenylidene" (in this case phenyldindenylidene).

15 Also ligated to metal atom  $M$  are ligands  $X$  and  $X^1$  which are anionic ligands, shown in Figs. 1A, 1B and 1C. Such anionic ligands include those independently chosen from halogen, benzoate,  $C_1$ - $C_5$  carboxylate,  $C_1$ - $C_5$  alkoxy, phenoxy, and  $C_1$ - $C_5$  alkylthio groups. In other particular 20 embodiments,  $X$  and  $X^1$  are each halide,  $CF_3CO_2$ ,  $CH_3CO_2$ ,  $CFH_2CO_2$ ,  $(CH_3)_3CO$ ,  $(CF_3)_2(CH_3)CO$ ,  $(CF_3)(CH_3)_2CO$ ,  $PhO$ ,  $MeO$ ,  $EtO$ , tosylate, mesylate, brosylate, or trifluoromethanesulfonate. In other particular 25 embodiments, both  $X$  and  $X^1$  are chloride. Ligands  $X$  and  $X^1$  can further be bonded to each other, forming a bidentate anionic ligand. Examples include diacid salts, such as dicarboxylate salts. As discussed herein, such groups can alternatively be further bound to a solid phase, for example a polymer support.

30 Also ligated to metal atom  $M$  are ligands  $L$  and  $L^1$ . These ligands are chosen from a number of different chemical classes.

One of these classes of ligands  $L$  or  $L^1$  is the 35 class of nucleophilic carbenes. In the inventive catalytic complexes, at least one of the ligands  $L$  or  $L^1$

is a member of this class. Nucleophilic carbenes are those molecules having a carbon atom which bears a lone pair of electrons, desirably also including those molecules additionally having electron-withdrawing character manifested in atoms or substituents in electronic communication with, or bonded to, the carbon bearing the lone pair. Such electron withdrawing atoms or substituents can include atoms which are more electronegative than carbon, such as nitrogen, oxygen, and sulfur. These atoms can either be bonded directly to the carbene carbon, or in a conjugated or hyperconjugated position with respect to this carbon. Substituents which have electron-withdrawing character include nitro, halogen, sulfonate, carbonate, sulfide, thioether, cyano, and other groups known to those in the art.

In particular embodiments, it has been found to be desirable that not both of ligands L and L<sup>1</sup> be nucleophilic carbenes, although embodiments in which both L and L<sup>1</sup> are nucleophilic carbenes are also operative.

Particularly desirable are nucleophilic carbene ligands further substituted with substituents which increase the steric crowding around the carbon bearing the lone pair of electrons. These groups can be bonded directly to the carbene carbon, within a few atoms of the carbene carbon, or remotely from the carbene carbon, as long as the bulky group is able to inhibit the approach of agents which tend to react with, and destroy the carbene, and consequently disable the catalytic complex as a whole. Thus the stability of the nucleophilic carbene ligand, and the catalyst itself are fostered by the presence of bulky groups which are able to shield the nucleophilic carbene from reaction. It should be noted that the olefin metathesis active carbene fragment is sterically protected from bimolecular decomposition by

the large steric umbrella provided by the bulky nucleophilic carbene ligand.

Although the invention is not limited by any particular mechanistic theory, it is believed that such a substituent arrangement can provide steric protection from carbene degradation pathways, including thermally induced degradation. The steric bulk of nucleophilic ligands as described herein can lead to more thermally stable catalysts. Such bulky or sterically hindering groups include branched alkyl groups, aryl groups, and aryl groups having branched alkyl substituents, particularly at the ortho positions of the aryl rings. For example, a nucleophilic carbene ligand having bulky alkyl groups such as tert-butyl, iso-propyl or aryl groups with bulky alkyl groups such as 2,4,6-trialkylphenyl or 2,6-dialkylphenyl interacting with the carbene, could be employed in the present invention. The groups L and L<sup>1</sup> can also be further bonded to each other, forming a bidentate ligand wherein either one or both of L and L<sup>1</sup> are nucleophilic carbene ligands.

Cyclic nucleophilic carbene ligands are also envisioned. These may have heteroatoms either in the ring, or bonded to the ring. Particularly desirable examples of this type of nucleophilic carbene ligand are those ligands having a carbene carbon between heteroatoms. Examples include dinitrogen rings such as imidazole, disulfur rings such as 1,3-dithiolane, and dioxygen rings such as 2H,4H-1,3-dioxine. The aromatic, non-aromatic, saturated or unsaturated analogs can be used as well.

Fig. 2A depicts an example of a nucleophilic carbene ligand which can be utilized in certain embodiments of the present invention. Shown is an imidazol-2-ylidene having substituents Y and Y<sup>1</sup>, and Z and Z<sup>1</sup>. Each substituent is independently selected from a

number of carbon-containing groups, or from hydrogen. The carbon-containing groups which can comprise Y, Y<sup>1</sup>, Z and Z<sup>1</sup> include alkyl groups having from 1 to 20 carbon atoms (such as methyl, ethyl, n-propyl, iso-propyl, n-butyl, iso-butyl, sec-butyl, and the like). Also possible are alkenyl or alkynyl substituents having from 2 to 20 carbon atoms. The groups can also include alkoxy carbonyl substituents having from 2 to 20 carbons atoms, aryl groups, carboxylate substituents having from 10 1 to 20 carbon atoms, alkoxy substituents having from 1 to 20 carbon atoms, alkenyloxy or alkynyloxy substituents having from 2 to 20 carbon atoms, as well as aryloxy substituents. Each of the above classes of substituent can be further optionally substituted with halogen, or 15 with alkyl or alkoxy groups of from 1 to 5 carbon atoms.

Any of the above substituents can include all structural isomers (n-, iso-, sec-, and tert-), cyclic or polycyclic isomers, and multiply unsaturated variants. It should also be noted that the presence of the double 20 bond in the imidazole ring is not required for catalytic activity in the present invention. In certain embodiments, an imidazolidin-2-ylidene can be used as nucleophilic carbene ligand L or L<sup>1</sup>.

The structure in Fig. 2B is a particular example 25 of a useful nucleophilic carbene ligand, having both Y and Y<sup>1</sup> as 2,4,6-trimethylphenyl, and both Z and Z<sup>1</sup> as hydrogen. This particular ligand is referred to as 1,3-bis(2,4,6-trimethylphenyl)imidazol-2-ylidene, or IMes. Another example of a useful nucleophilic carbene is given 30 in Fig. 2C, which shows a structure having both Y and Y<sup>1</sup> as 2,6-diisopropylphenyl, and both Z and Z<sup>1</sup> as hydrogen. This particular ligand is referred to as 1,3-bis(2,6-diisopropylphenyl)imidazol-2-ylidene, or IPr.

Another class of ligand which can serve as L or L<sup>1</sup> 35 is the class of phosphines. Particularly useful are

trialkyl- or triarylphosphines, such as trimethylphosphine, triphenylphosphine, triisopropylphosphine, and similar phosphines. The phosphines tricyclohexylphosphine and 5 tricyclopentylphosphine are also useful, and are collectively referred to as PCy<sub>3</sub>.

Other classes of ligands which can serve as L or L<sup>1</sup> are sulfonated phosphines, phosphites, phosphinites, phosphonites, arsine, stibine, imines, ethers, amines, 10 amides, sulfoxides, carbonyls, carboxyls, nitrosyls, pyridines, and thioethers.

Other embodiments of catalytic complexes useful in the present invention are shown in Figs. 3A (alkylidene), 3B (vinylidene) and 3C (allenylidene), in which the 15 analogy with the series of Figs. 1A, 1B and 1C is based on the identity of the olefin metathesis active carbene ligand, alkylidene, vinylidene and allenylidene, respectively. The elements M, X, C<sup>1</sup>, C<sup>2</sup>, C<sup>3</sup>, R and R<sup>1</sup> are as described above for the first described embodiment of 20 the inventive catalytic complex. In this second particular embodiment, ligand L is a nucleophilic carbene ligand, as described above. In addition, since the species depicted in Figs. 3A, 3B, and 3C are all cationic complexes, an anion A<sup>-</sup> is required. This anion can be any 25 inorganic anion, and can also include some organic anions. Thus, A<sup>-</sup> can be, for example, halide ion, SbF<sub>6</sub><sup>-</sup>, PF<sub>6</sub><sup>-</sup>, BF<sub>4</sub><sup>-</sup>, AsCl<sub>4</sub><sup>-</sup>, O<sub>3</sub>SONO<sup>-</sup>, SO<sub>2</sub>F<sup>-</sup>, NSO<sub>3</sub><sup>-</sup>, azide, nitrite, nitrate, or acetate, and many others known to those of skill in the art.

30 In this embodiment, another ligand of metal M is Ar, which is an aromatic ring system, including the η<sup>6</sup>-bonded system. The symbol η is used to signify that all aromatic ring atoms are bonded to the metal atom. Such systems include C<sub>6</sub>H<sub>6</sub> ring systems, and various alkyl 35 substituted C<sub>6</sub>H<sub>6</sub> ring systems. Heterocyclic arene rings

are also suitable, and these include  $\eta^6$ -C<sub>5</sub>H<sub>5</sub>N, and alkyl substituted derivatives thereof. These rings can have substituents chosen from a wide range of groups including alkyl groups having from 1 to 20 carbon atoms (such as 5 methyl, ethyl, n-propyl, iso-propyl, n-butyl, iso-butyl, sec-butyl, and the like). Also possible are alkenyl or alkynyl substituents having from 2 to 20 carbon atoms. The groups can also include alkoxy carbonyl substituents having from 2 to 20 carbons atoms, aryl groups, 10 carboxylate substituents having from 1 to 20 carbon atoms, alkoxy substituents having from 1 to 20 carbon atoms, alkenyloxy or alkynyoxy substituents having from 2 to 20 carbon atoms, as well as aryloxy substituents. Each of the above classes of substituent can be further 15 optionally substituted with halogen, or with alkyl or alkoxy groups of from 1 to 5 carbon atoms. For example, useful  $\eta^6$ -bonded L or L<sup>1</sup> ligands are p-cymene, fluorene and indene.

The inventive catalytic complexes can be used as 20 homogeneous catalysts, or are equally well suited as heterogeneous catalysts. The latter embodiment is realized by linking the catalytic complexes to a suitable solid phase, such as a polymeric support. The solid phase can be bound to the catalytic complex either 25 cleavably or non-cleavably. The solid phase can be a polymer which can either be a solid-state resin such as a Wang resin, or a soluble polymer such as non-crosslinked chloromethylated polystyrene (NCPS). This polymer shows excellent properties, such as solubility in 30 tetrahydrofuran (THF), dichloromethane, chloroform, and ethyl acetate, even at low temperatures (-78°C). NCPS is insoluble in water and methanol. These features allow traditional organic chemistry techniques such as solvent extraction, and methanol precipitation. Suitable

polymers include hydroxyl-containing polymers such as Wang resin, or poly(ethylene glycol) (PEG).

The method of attachment between solid phase and catalytic complex can take the form of a link to the 5 ligand L or L<sup>1</sup>, which is desirably the nucleophilic carbene ligand. This arrangement is desirable since the catalytic complex is believed to operate by first releasing the ligand which is not a nucleophilic carbene, for example, by releasing a phosphine ligand. Thus, 10 linkage to the phosphine ligand would result in loss of the solid phase-catalytic complex interaction, upon catalysis. Also considered desirable is linkage of the catalytic complex to a solid phase through the anionic ligands X and/or X<sup>1</sup>. Thus, any linkage which involves a 15 group serving as an anionic ligand as described above can be used to attach the catalytic complex to a solid support. For example, carboxylate resins can be employed for this purpose.

The inventive catalytic complexes are air- and 20 moisture-stable, and thus can be used under atmospheric conditions, and even in aqueous environments. The stability of the catalytic substrates and products will be the limiting factors with respect to use under such conditions. The inventive catalytic complexes are soluble 25 in typical organic solvents, such as tetrahydrofuran (THF), benzene, toluene, xylene, diethyl ether, dioxane, alcohols, acetonitrile, dimethylsulfoxide (DMSO), dimethylformamide (DMF), and similar solvents, but not particularly soluble in water or methanol.

30 The catalytic complexes need not be used in the presence of any initiators or cocatalysts, although materials such as phosphine sponges can optionally be used. Those of skill in the art will recognize the identity of the members of this class, which includes 35 copper chloride, and Lewis acids generally, in

concentrations up to those stoichiometric with that of the catalytic complex.

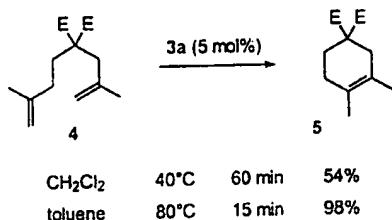
Use of Catalytic Complexes in Ring-Closing Metathesis

5    (RCM)

The catalytic complexes can be used for ring-closing metathesis. This reaction converts a diterminal diene (a compound having two  $-C^a=C^bH_2$  groups, the  $C^a$  atoms of which are able to link together to form a cyclic compound with 10 a  $-C^a=C^a-$  linkage), to a cyclic alkene, with  $H_2C^b=C^bH_2$  as a side product. In some instances, the diterminal diene (or an  $\alpha, \omega$  diene) can undergo a 1,3-hydrogen shift rearrangement (to give an  $\alpha, \omega-1$  diene), and the product will be a cyclic alkene with one less methylene group in 15 the ring, and propene as a side product.

A pronounced solvent dependence of the reactivity of the present catalytic complexes was noticed. As can be seen from the results compiled in Scheme 1, reaction rates for  $(IMes)(Pcy_3)Cl_2Ru(=CHPh)$  in toluene are 20 substantially higher than those in  $CH_2Cl_2$  (the substituent E is  $-CO_2Et$ ). Thus, the tetrasubstituted cyclohexene derivative of Scheme 1 is formed in essentially quantitative yield after only 15 min if the reaction is carried out in toluene. The reaction requires 2-3 hours 25 in  $CH_2Cl_2$  to reach completion. This influence of the reaction medium has been observed for the ruthenium carbene complexes bearing N-mesityl substituents on their imidazol-2-ylidene ligands. However, the related complexes having N-cyclohexyl or N-isopropyl groups do 30 not show this effect.

**Scheme 1. Solvent Dependence of the Reactivity of Complex (IMes)(Pcy<sub>3</sub>)Cl<sub>2</sub>Ru(=CHPh)**

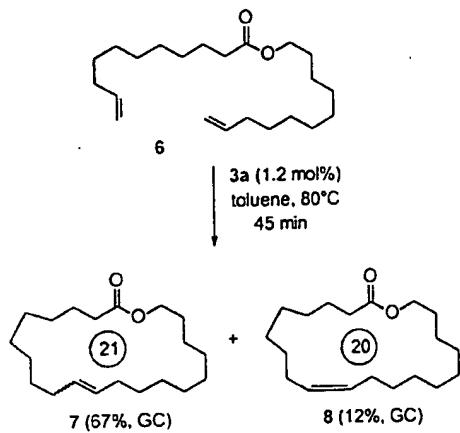


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This reactivity of (IMes)(Pcy<sub>3</sub>)Cl<sub>2</sub>Ru(=CHPh) in toluene is impaired by a tendency of the active species to promote isomerization of the double bonds of the substrate. Thus, in Scheme 2, treatment of the pictured diene with as little as 1.2 mol% of (IMes)(Pcy<sub>3</sub>)Cl<sub>2</sub>Ru(=CHPh) in toluene leads to complete consumption of the starting material within 45 min, but delivers significant amounts of the 20-membered ring in addition to the desired 21-membered lactone. Although not wishing to be bound by any particular theory, the cis-cyclic alkene is believed to result from an initial isomerization of one of the double bonds in the starting material, followed by elimination of propene instead of ethylene during ring closure. This intrinsic bias for ring contraction was not suppressed by lowering the reaction temperature. In stark contrast, however, only minute amounts of the cis-alkene are detected if the reaction is performed in CH<sub>2</sub>Cl<sub>2</sub>.

25

Scheme 2. Stereochemistry



5 As can be seen from the results compiled in Table 1, the reactivities of  $(\text{IMes})(\text{Pcy}_3)\text{Cl}_2\text{Ru}(\text{=CHPh})$  and  $(\text{IMes})(\text{Pcy}_3)\text{Cl}_2\text{Ru}(\text{phenylindenylidene})$  in  $\text{CH}_2\text{Cl}_2$  are sufficiently high to allow the preparation of di-, tri- and even tetrasubstituted cyclo-alkenes in good to 10 excellent yields. All ring sizes including medium and macrocyclic ones can be accessed. The yield data given are the isolated yields. The reactions with yields given with superscript b (entries 1-4) were carried out in toluene at 80°C. The compound 3a refers to 15  $(\text{IMes})(\text{Pcy}_3)\text{Cl}_2\text{Ru}(\text{=CHPh})$ , and 3b to  $(\text{IMes})(\text{Pcy}_3)\text{Cl}_2\text{Ru}(\text{phenylindenylidene})$ . E is  $-\text{CO}_2\text{Et}$ .

**Table 1.** RCM catalyzed by (IMes)(Pcy<sub>3</sub>)Cl<sub>2</sub>Ru(=CHPh) and (IMes)(Pcy<sub>3</sub>)Cl<sub>2</sub>Ru(phenylindenylidene) in CH<sub>2</sub>Cl<sub>2</sub>.

Entry	Product	Catalyst (mol%)	Yield (%)
1		3a (2%)	96 <sup>b</sup>
2		3b (2%)	97 <sup>b</sup>
3		3a (5%) (E=CO2Et)	77 <sup>b</sup>
4		3b (2%)	89 <sup>b</sup>
5		3a (5%)	98
6		3a (5%)	93
7		3b (5%)	71
8		3a (1%)	64
9		3a (1%) 3a (5%)	62 (R = H) 95 (R = Me)
10		3a (2%)	72
11		3a (3%)	82
12		3a (4%)	71

5 It must be noted that most of these cyclizations cannot be carried out if the bis(phosphine) complex (PCy<sub>3</sub>)<sub>2</sub>Cl<sub>2</sub>Ru(=CHPh) is used as the catalyst. This holds true for all tetrasubstituted cases (entries 1-4 and 7),

the trisubstituted 8-membered ring shown in entry 10, as well as for annulation reactions depicted in entries 5 and 6. Although the macrocyclic products (entries 11-13) can also be obtained with the use of  $(PCy_3)_2Cl_2Ru(=CHPh)$ , using  $(IMes)(PCy_3)Cl_2Ru(=CHPh)$  results in shorter reaction times and allows lower catalyst loadings to be employed. This aspect is particularly relevant with respect to pentadec-10-enolide (entry 11) which is converted into the valuable, musk-odored perfume ingredient EXALTOLIDE<sup>®</sup> ( = pentadecanolide) upon simple hydrogenation.

As can be deduced from the results in Table 1, complex  $(IMes)(PCy_3)Cl_2Ru(=CHPh)$  bearing a benzylidene carbene moiety and complex  $(IMes)(PCy_3)Cl_2Ru(\text{phenylindenylidene})$  with a phenylindenylidene unit are essentially equipotent pre-catalysts.

Method of Making Catalytic Complexes

20 The inventive catalytic complexes can be made according to the following general synthetic procedures, which are adapted from known procedures.

25 To synthesize a catalytic complex according to a first embodiment of the invention, one of the two phosphine ligands of a diphosphine-ligated ruthenium or osmium catalyst is exchanged with a nucleophilic carbene ligand. For example, starting material diphosphine-ligated complexes  $(PCy_3)Cl_2Ru(=CHPh)$  and  $(PPh_3)Cl_2Ru(=CHPh)$  can be synthesized according to general procedures such as those given by Schwab et al., *Angew. Chem. Int'l. Ed. Engl.*, (1995) 34, 2039-41.

30 Ligand-exchange reactions are carried out by exposing the diphosphine-ligated complexes to nucleophilic carbene ligands, as defined above, in

suitable solvents such as THF, toluene, and the like. Reactions are generally carried out at temperatures of from about 0°C to about 50°C, for about 15 minutes to several hours. Subsequent recrystallization in inert 5 solvents gives the complexes in good yield and high purity.

The nucleophilic carbene ligands according to the invention are synthesized according to the following general synthetic procedure. Solutions of heteroatom-10 containing starting material such as aniline, or substituted aniline, phenol or substituted phenol, benzenethiol or substituted benzenethiol, primary- or secondary-amines, alcohols and thiols can be prepared in solvents such as tetrahydrofuran (THF), benzene, toluene, 15 xylene, diethyl ether, dioxane, alcohols, acetonitrile, dimethylsulfoxide (DMSO), dimethylformamide (DMF), water, and similar solvents, under an inert atmosphere. Substituents for the above groups include alkyl groups having from 1 to 20 carbon atoms (such as methyl, ethyl, 20 n-propyl, iso-propyl, n-butyl, iso-butyl, sec-butyl, and the like). Also possible are alkenyl or alkynyl substituents having from 2 to 20 carbon atoms. The groups can also include alkoxy carbonyl substituents having from 2 to 20 carbons atoms, aryl groups, 25 carboxylate substituents having from 1 to 20 carbon atoms, alkoxy substituents having from 1 to 20 carbon atoms, alkenyloxy or alkynyoxy substituents having from 2 to 20 carbon atoms, as well as aryloxy substituents. Each of the above classes of substituent can be further 30 optionally substituted with halogen, or with alkyl or alkoxy groups of from 1 to 5 carbon atoms. Particularly useful are those substituents such as methyl, ethyl, propyl, and butyl, including branched isomers, and aryl substituents at the ortho- or diortho-positions (for 35 example, 2- or 2,6- substitution for benzyl rings).

The solution is then contacted with an approximately one half of equimolar amount (with respect to the heteroatom-containing starting material) of paraformaldehyde. After heating to dissolve 5 paraformaldehyde, the contents of the flask are acidified with an approximately one half of equimolar amount (with respect to the heteroatom-containing starting material) of mineral acid (for example, hydrochloric acid or nitric acid). 10 At this stage, if a nitrogen-containing starting material (aniline-derivative or primary amine-derivative) is used, an approximately one half of equimolar amount (with respect to the heteroatoms-containing starting material) of a dialkoxyacetaldehyde is added drop wise 15 after a few minutes of stirring. The dialkoxyacetaldehyde can be dimethoxy-, diethoxy-, dipropoxy-, dibutoxy-, diphenoxy, or can be any of a number of combinations of such alkoxy substituents such as for example methoxyethoxy, or methoxyphenoxy. The 20 procedure then continues as follows.

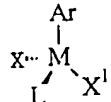
If, on the other hand, oxygen or sulfur heteroatom-containing starting material is used, the above paragraph is not followed, and the procedures from this point on are common to all starting materials.

25 After equipping the reaction flask with a Dean-Stark trap, or similar device, the mixture is heated to a temperature of from about 80°C to about 180°C, preferably from about 100°C to about 150°C for several hours (from about 5 to about 30 hours). During this time, a 30 precipitate forms, as the side products of water and methanol, as well as some solvent, are removed. The reaction mixture is stirred at room temperature for a time ranging from about 20 minutes to about 4 hours, preferably from 1 to 3 hours. Precipitate will have 35 formed during this time.

The precipitate is filtered, washed with a suitable solvent, such as THF to give the nucleophilic carbene product in the form of a salt. For example, if aniline or substituted aniline is used, the product will 5 be a 1,3-diarylimidazole salt. If the starting material is a primary amine, the product will be a 1,3-dialkyl imidazole salt. Either of these products can be converted to the saturated heterocyclic derivative (imidazolidine) by conventional hydrogenation techniques 10 such as exposure to H<sub>2</sub> over a carbon-palladium or carbon-platinum catalyst. Such techniques will be recognized and known to those of skill in the art. If the starting material is a phenol- or thiobenzene-derived compound, the product will be a dibenzoxymethane-, or 15 dibenzthiomethane-product. If the starting material is an alcohol or thiol, the product will be a 1,1-bis(alkoxy)methane- or 1,1-bis(alkylthio)methane-product.

The second embodiments of the catalytic complexes of the invention are easily made by combining a precursor 20 species of the catalytic complexes with an acetylene to give the allenylidene type of catalytic complex (see Fig. 3C). An example of this precursor species of the catalytic complex is shown below.

25



In this structure, metal M, and ligands X, X<sup>1</sup>, L and Ar are defined as above, with L being a nucleophilic 30 carbene. This precursor species is generally available in the form of a dimer [ArRuCl<sub>2</sub>]<sub>2</sub>, which is converted to the precursor species when the dimer is exposed to a nucleophilic carbene in a suitable solvent such as THF,

hexanes and other non-protic solvents. For example, the dimer [(p-cymene)-RuCl<sub>2</sub>]<sub>2</sub> is commercially available from Strem Chemicals (Newburyport, MA).

The acetylenes with which precursor species of the inventive catalytic complexes combine to form second embodiments of the invention are terminal acetylenes, and can be substituted at the  $\gamma$ -position with alkyl or aryl groups, or optionally further substituted with halogen, or with alkyl or alkoxy groups of from 1 to 10 carbon atoms, or aryl groups. Further substitution can include the functional groups of hydroxyl, thiol, thioether, ketone, aldehyde, ester, amide, amine, imine, nitro, carboxylic acid, disulfide, carbonate, isocyanate, carbodiimide, carboalkoxy, carbamate, and halogen. Particularly useful substituents are vinyl, phenyl, or hydrogen, wherein the vinyl and phenyl substituents are optionally substituted with one or more moieties selected from C<sub>1</sub>-C<sub>5</sub> alkyl, C<sub>1</sub>-C<sub>5</sub> alkoxy, phenyl or a functional group, such as chloride, bromide, iodide, fluoride, nitro, or dimethylamine.

The invention will be further described in the following examples, which do not limit the scope of the invention described in the claims.

25

#### Examples

Illustrations of methods of making certain embodiments of the inventive catalytic complexes, as well as properties thereof, are provided by the following examples.

30

##### Example 1: Synthesis of IMes-HCl

A 300 mL Schlenk flask was charged with 2,4,6-trimethylaniline (10g, 74 mmol), toluene (50 mL), and paraformaldehyde (1.11 g, 37 mmol) under argon and heated to 110°C until all the paraformaldehyde was dissolved.

35

The flask was then cooled to 40°C and HCl (6.17 mL, 6N, 37 mmol) was added to the reaction mixture drop wise. The mixture was stirred at that temperature for 10 minutes before dimethoxyacetaldehyde (6.442 g, 60% wt. in water, 37 mmol) was added in drop wise fashion. The 5 flask was then equipped with a Dean-Stark trap and heated to 120°C for 15 hours, during which time a dark precipitate was formed and grew in volume by removal of the side-products (H<sub>2</sub>O and methanol) and some of the 10 solvent through the Dean-Stark trap. The reaction mixture was then allowed to cool to room temperature and stirred at that temperature for two hours. Filtration of the precipitate through a Schlenk frit, washing with tetrahydrofuran (three times, 20 mL each wash), and 15 drying yielded a white solid in 60% yield, which was characterized spectroscopically as pure IMes-HCl. <sup>1</sup>H NMR: δ = 2.12 (s, 12H, o-CH<sub>3</sub>), 2.30 (s, 6H, p-CH<sub>3</sub>), 6.97 (s, 4H, mesityl), 7.67 (s, 2H, NCH<sub>2</sub>CHN), 10.68 (s, 1H, HCl).

20

Example 2: Synthesis of IMes

In a glovebox, a 300 mL Schlenk flask equipped with a stir bar was charged with 20.0g (58.7 mmol) of IMes-HCl and 120 mL of dry tetrahydrofuran. The 25 resulting suspension was stirred for 10 minutes after which time 6.80 g (60.7 mmol) of solid potassium tert-butoxide was added to the suspension at room temperature in a single portion. A dark gray solution was obtained immediately. The flask was taken out of the glovebox and 30 connected to the Schlenk line. The solution was stirred for 20 minutes before all volatiles were removed under vacuum. The residue was extracted into warm toluene (120 mL + 60 mL + 20 mL) and filtered through a medium porosity frit (filtration was rather slow), and the 35 solvent was removed under vacuum to obtain crystals of

IMes. The resulting product was recovered in 90% yield, and had a dark tint but was sufficiently pure for its use in further synthesis. Further purification could be achieved by recrystallization from toluene or hexane, 5 yielding colorless crystals.

The synthesis of related carbenes 1,3-bis(4-methylphenyl)imidazol-2-ylidene (ITol) and 1,3-bis(4-chlorophenyl)imidazol-2-ylidene (IpCl) was carried in an analogous fashion.

10

Example 3: Synthesis of (IMes)(PCy<sub>3</sub>)(Cl)<sub>2</sub>Ru(=CHCH=CMe<sub>2</sub>)

The procedure was carried out under purified and dried argon atmosphere and with dried and degassed solvents. IMes (2.1990 g, 7.221 mmol) was suspended in 15 250 mL hexanes, into which (Cl)<sub>2</sub>(PCy<sub>3</sub>)<sub>2</sub>Ru(=CHCH=CMe<sub>2</sub>) (5.0718 g, 7.092 mmol) was added in one portion. The mixture was heated for 2.5 hours with stirring at 60°C. During this period, the formation of an orange-brown precipitate was observed. The volume of the suspension 20 was then reduced in vacuum to 50 mL and the suspension was cooled to -78°C. Following filtration and cold pentane washing of the residue (2 washes, each 20 mL), the product was isolated as a brown orange microcrystalline material in 72% yield (3.97g).

25

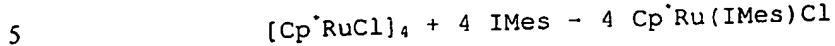
Example 4: Synthesis of (IMes)(PCy<sub>3</sub>)Cl<sub>2</sub>Ru(=CHPh)

The procedure of Example 3 was followed, except that (Cl)<sub>2</sub>(PCy<sub>3</sub>)<sub>2</sub>Ru(=CHPh) was used. This complex was soluble in a variety of organic solvents including 30 hydrocarbon, tetrahydrofuran, acetone, methylene chloride, and diethylether. The identity of the complex was confirmed by X-ray crystallography. Other embodiments will be readily synthesized by substituting the IMes ligand with other nucleophilic carbene ligands.

35

Example 5: Thermodynamic Studies

The thermodynamics of the following reaction in tetrahydrofuran (THF) at room temperature were studied.



( $\text{Cp}^*$  is  $\eta^5\text{-C}_5\text{Me}_5$ ) The reaction proceeds rapidly as indicated by the rapid development of a deep blue color in the reaction solution. A deep blue crystalline solid 10 was isolated in 86% yield. Nuclear magnetic resonance data of the blue solid indicated the isolation of a single species bearing a unique  $\text{Cp}^*$  and a single carbene ligand. X-ray crystallography confirmed the formulation of  $\text{Cp}^*\text{Ru}(\text{IMes})\text{Cl}$ . An enthalpy of reaction of  $-62.6 \pm 0.2$  15 kcal/mol was measured by anaerobic solution calorimetry in THF at 30°C when 4 equivalents of carbene were reacted with 1 equivalent of the tetramer,  $[\text{Cp}^*\text{RuCl}]_4$ . Table 1 compares the enthalpy of similar reactions where IMes is replaced with other moieties.

20

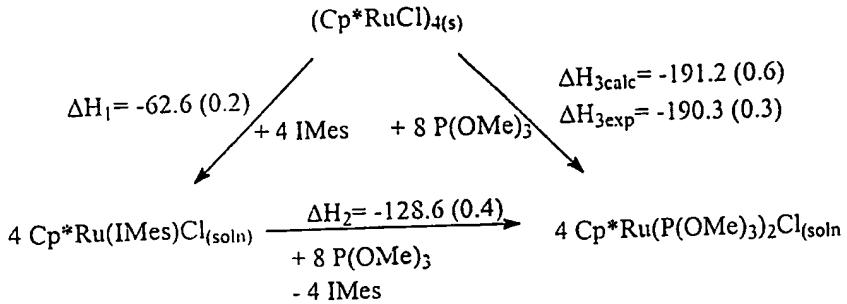
Table 1. Comparison of Reaction Enthalpies

Identity of L in $\text{Cp}^*\text{Ru}(\text{L})\text{Cl}$	$\Delta H$ (kcal/mol) of reaction: $[\text{Cp}^*\text{RuCl}]_4 + 4 \text{ L} \rightarrow 4 \text{ Cp}^*\text{Ru}(\text{L})\text{Cl}$	Relative stability of Ru-L bond (kcal/mol)
IMes	$-62.6 \pm 0.2$	-15.6
$\text{P}(\text{isopropyl})_3$	$-37.4 \pm 0.3$	-9.4
$\text{P}(\text{cyclohexyl})_3$	$-41.9 \pm 0.2$	-10.5

25 The IMes ligand proves to be a stronger binder to the  $\text{Cp}^*\text{RuCl}$  fragment than  $\text{PCy}_3$ , by 5 kcal/mol. The carbene ligand is a fairly good binder but can be displaced if a better donor ligand, such as a phosphite,

is used. The phosphite reaction allows for the construction of a thermochemical cycle which confirms the internal consistency of the calorimetric data, as shown in Scheme 1.

5 Scheme 1. Thermodynamic Cycle



10 A further verification of the thermochemical results can be made by examining the following hypothetical reaction.



15 This reaction is calculated to be exothermic by 5 kcal/mol and no entropic barrier is apparent, so the reaction should proceed readily as written. Indeed, upon mixing of the reagents in THF-d<sub>6</sub>, the characteristic <sup>31</sup>P signal of Cp<sup>\*</sup>Ru(PCy<sub>3</sub>)Cl disappears (at 11.3 ppm), and that of free PCy<sub>3</sub> appears (40.4 ppm), as observed by Campion et al., *J. Chem. Soc. Chem. Commun.*, (1988) 278-280.

Example 6: Structural Studies

20 In order to gauge the steric factor inherent in the catalytic systems, structural studies were carried out on Cp<sup>\*</sup>Ru(IMes)Cl (Fig. 4), Cp<sup>\*</sup>Ru(PCy<sub>3</sub>)Cl (Fig. 5), and (IMes)(PCy<sub>3</sub>)Cl<sub>2</sub>Ru(=CHPh) (Fig. 6). Comparison was made to another sterically demanding ligand in the complex

$\text{Cp}^*\text{Ru}(\text{P}^i\text{Pr}_3)\text{Cl}$ . The following crystal data was obtained.

For  $\text{Cp}^*\text{Ru}(\text{IMes})\text{Cl}$ : monoclinic, space group  $\text{P}2_1/c$ , dark

blue prism,  $0.35 \times 0.25 \times 0.20$ ,  $a = 10.6715$  (2),  $b =$

14.3501 (3),  $c = 19.2313$  (4),  $\beta = 103.2670$  (10) deg,  $z = 4$ ,

5  $R_f = 0.0294$ , GOF = 0.888. For  $\text{Cp}^*\text{Ru}(\text{PCy}_3)\text{Cl}$ : orthorhombic,

space group  $\text{Pcba}$ , dark blue prism,  $0.45 \times 0.35 \times 0.25$ ,  $a =$

18.9915 (6),  $b = 15.6835$  (5),  $c = 19.0354$  (6),  $z = 8$ ,  $R_f =$

0.0392, GOF = 1.132. For  $(\text{IMes})(\text{PCy}_3)\text{Cl}_2\text{Ru}(-\text{CHPh})$ : space

group  $\text{P}2_1\text{2}_1\text{2}_1$ , yellow-orange prism,  $a = 12.718$  (1),  $b =$

10  $c = 14.549$  (1),  $R_f = 0.0616$ ,  $z = 4$ , GOF = 1.038.

The metrical data of  $\text{Cp}^*\text{Ru}(\text{P}^i\text{Pr}_3)\text{Cl}$  (Campion et al., *J. Chem. Soc. Chem. Commun.*, (1988) 278-280) can be used for comparison: Ru-P, 2.383 (1) Å; Ru-Cl, 2.378

(1) Å; Ru- $\text{Cp}^*(\text{c})$ , 1.771 (1) Å; Cl-Ru-P, 91.2 (1) °; Cl-Ru-

15  $\text{Cp}^*(\text{c})$ , 129.9 (1) °; C(1)-Ru- $\text{Cp}^*(\text{c})$ , 139.9 (1) °.

The three  $\text{Cp}^*\text{RuCl}(\text{L})$  structures are similar, with

the variation in Ru-L distances the only standout

feature, but this is explainable by the difference in

covalent radii between P and C. Only slight angle

20 distortions are observed in  $\text{Cp}^*\text{Ru}(\text{IMes})\text{Cl}$ , presumably to

accommodate the bulkiness of IMes. The IMes ligand

displays non-coplanar rings with torsion angles of 78.46

(4) ° between the arene ring bound to N(2) and the

imidazole ring and 78.78 (5) ° between the imidazole ring

25 and the arene ring bound to N(1). The two arene rings

adopt a mutually staggered configuration.

A direct comparison of the steric properties

displayed by IMes and PCy<sub>3</sub> provides insight into the

30 significant steric congestion provided by the IMes

ligation. The cone angle reported for  $\text{P}^i\text{Pr}_3$  and PCy<sub>3</sub> are

160° and 170°, respectively (Tolman, *Chem. Rev.* (1977) 77,

313-348). Such a cone angle measurement is not

straightforward in the present system. Instead, the

35 crystallographic data can be used to determine closest

contact angles involving non-hydrogen atoms in

$\text{Cp}^*\text{Ru}(\text{IMes})\text{Cl}$  and  $\text{Cp}^*\text{Ru}(\text{PCy}_3)\text{Cl}$ . For the  $\text{Ru-PCy}_3$  fragment, an angle of  $96.3^\circ$  is measured using cyclohexyl methylene carbons on adjacent cyclohexyl rings defining the largest angle. For the  $\text{Ru-P}^i\text{Pr}_3$  fragment in  $\text{Cp}^*\text{Ru}(\text{P}^i\text{Pr}_3)\text{Cl}$  a similar angle of  $95.8^\circ$  is obtained. As for the IMes fragment, two parameters can be obtained. Angles of  $150.7^\circ$  and  $115.3^\circ$  are measured for the  $\langle 4\text{-Me-Ru-4}'\text{-Me}$  and  $\langle 6\text{-Me-Ru-2}'\text{-Me}$  angles, respectively. The steric coverage of the IMes ligand can be considered as a fence rather than a cone. The increased steric congestion provided by the IMes ligand compared to  $\text{PCy}_3$  derives from the presence of bulky substituents on the imidazole nitrogens and, to a greater extent, from the significantly shorter metal-carbon bond distance which brings the entire IMes ligand closer to the metal center.

The structural analysis of  $(\text{IMes})(\text{PCy}_3)\text{Cl}_2\text{Ru}(=\text{CHPh})$  shown in Fig. 6 reveals a distorted square pyramidal coordination with a nearly linear  $\text{Cl}(1)\text{-Ru-Cl}(2)$  angle ( $168.62^\circ$ ). The carbene unit is perpendicular to the  $\text{C}(1)\text{-Ru-P}$  plane, and the carbene aryl moiety is only slightly twisted out of the  $\text{Cl}(1)\text{-Ru-Cl}(2)\text{-C}(40)$  plane. The  $\text{Ru-C}(40)$  bond distance ( $1.841$   $11\text{\AA}$ ) is the same as that in  $\text{RuCl}_2(=\text{CH-}p\text{-C}_6\text{H}_4\text{Cl})(\text{PCy}_3)_2$  ( $1.838$  (3)  $\text{\AA}$ ) and shorter than that in  $(\text{PCy}_3)_2\text{RuCl}_2(=\text{CHCH=CPH}_2)$  ( $1.851$  (21)  $\text{\AA}$ ). While two (formally) carbene fragments are present in  $(\text{IMes})(\text{PCy}_3)\text{Cl}_2\text{Ru}(=\text{CHPh})$ , they display different  $\text{Ru-C}$  distances ( $\text{Ru-C}(40)= 1.841$  (11) and  $\text{Ru-C}(1)= 2.069$  (11)  $\text{\AA}$ ). These important metrical parameters clearly distinguish two metal-carbene interactions: a metal benzylidene fragment with a formal metal to carbon double bond and a metal imidazolium carbene with a formal metal-carbon single bond. From Fig. 6, it is also clear that the IMes ligand is sterically more demanding than  $\text{PCy}_3$ .

Example 7: Thermal Stability Studies

In the course of catalytic testing, the remarkable air stability of the inventive catalytic complexes was observed. To gauge the robust nature of these carbene complexes in solution, their thermal stability under inert atmosphere was tested at 60°C. The relative order of stability found was (IMes)(PCy<sub>3</sub>)Cl<sub>2</sub>Ru(=CHPh) >> (IMes)(PPh<sub>3</sub>)Cl<sub>2</sub>Ru(=CHPh) > (PCy<sub>3</sub>)<sub>2</sub>Cl<sub>2</sub>Ru(=CHPh). After 14 days of continuous heating of toluene solutions of (IMes)(PCy<sub>3</sub>)Cl<sub>2</sub>Ru(=CHPh) to 60°C, no decomposition was detected (as monitored by both <sup>1</sup>H and <sup>31</sup>P NMR). In contrast, solutions of (PCy<sub>3</sub>)<sub>2</sub>Cl<sub>2</sub>Ru(=CHPh) showed signs of decompositions after one hour, under the same conditions.

The catalyst (IMes)(PCy<sub>3</sub>)Cl<sub>2</sub>Ru(=CHPh) was stable at 100°C for 36 hours before showing any indication of decomposition. Similar thermal decomposition studies have been conducted in refluxing methylene chloride, dichloromethane, toluene, benzene and diglyme with similar results.

Other Embodiments

It is to be understood that while the invention has been described in conjunction with the detailed description thereof, the foregoing description is intended to illustrate and not limit the scope of the invention, which is defined by the scope of the appended claims. Other aspects, advantages, and modifications are within the scope of the following claims.

What is claimed is:

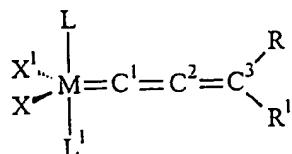
- 1 1. A catalytic complex comprising:
  - 2 a) a metal atom selected from the group
  - 3 consisting of ruthenium or osmium;
  - 4 b) at least one anionic ligand ligated to said
  - 5 metal;
  - 6 c) at least one nucleophilic carbene ligand
  - 7 ligated to said metal;
  - 8 d) a further ligand ligated to said metal; and
  - 9 e) a carbon-containing ligand ligated to said
  - 10 metal, wherein said carbon-containing ligand is
  - 11 selected from the group consisting of
  - 12 alkylidene, benzylidene, indenylidene, vinylidene,
  - 13 and allenylidene.
- 1 2. The catalytic complex of claim 1, wherein the anionic
- 2 ligand is selected from the group consisting of halide,
- 3 carboxylate, alkoxy, aryloxy, and alkyl sulfonate.
- 1 3. The catalytic complex of claim 2, wherein the anionic
- 2 ligand is chloride.
- 1 4. The catalytic complex of claim 1, wherein the
- 2 nucleophilic carbene ligand comprises a carbene carbon
- 3 further bonded to two heteroatoms having
- 4 electronegativity greater than that of carbon, wherein
- 5 the heteroatoms are independently selected from the group
- 6 consisting of nitrogen, oxygen, and sulfur.
- 1 5. The catalytic complex of claim 4, wherein the
- 2 nucleophilic carbene ligand comprises a substituted or
- 3 unsubstituted, saturated or unsaturated 1,3-
- 4 diheteroatomic cyclic compound.
- 1 6. The catalytic complex of claim 1, wherein the complex
- 2 is linked to a solid support by means of a link between
- 3 said anionic ligand and said solid support.

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1 7. The catalytic complex of claim 1, wherein the complex  
 2 is linked to a solid support by means of a link between  
 3 said nucleophilic carbene and said solid support.

1 8. The catalytic complex of claim 1, wherein the carbon-  
 2 containing ligand selected from the group consisting of  
 3 alkylidene, vinylidene and allenylidene is further  
 4 substituted with substituents selected from the group  
 5 consisting of hydrogen, C<sub>1</sub>-C<sub>20</sub> alkyl, C<sub>2</sub>-C<sub>20</sub> alkenyl, C<sub>2</sub>-C<sub>20</sub>  
 6 alkynyl, C<sub>2</sub>-C<sub>20</sub> alkoxy carbonyl, aryl, C<sub>1</sub>-C<sub>20</sub> carboxylate,  
 7 C<sub>1</sub>-C<sub>20</sub> alkoxy, C<sub>2</sub>-C<sub>20</sub> alkenyloxy, C<sub>2</sub>-C<sub>20</sub> alkynylloxy, and  
 8 aryloxy, optionally being substituted with C<sub>1</sub>-C<sub>5</sub> alkyl,  
 9 halogen, C<sub>1</sub>-C<sub>6</sub> alkoxy, or with a phenyl group substituted  
 10 with halogen, C<sub>1</sub>-C<sub>5</sub> alkyl or C<sub>1</sub>-C<sub>5</sub> alkoxy.

1 9. A catalytic complex of the formula:



2  
 3 wherein M is Os or Ru;  
 4 C<sup>1</sup>, C<sup>2</sup> and C<sup>3</sup> are sp<sup>2</sup>-hybridized carbons, wherein  
 5 either or both of C<sup>1</sup> and C<sup>2</sup> are optionally absent;  
 6 R and R<sup>1</sup> are independently selected from the group  
 7 consisting of hydrogen, C<sub>1</sub>-C<sub>20</sub> alkyl, C<sub>2</sub>-C<sub>20</sub> alkenyl, C<sub>2</sub>-C<sub>20</sub>  
 8 alkynyl, C<sub>2</sub>-C<sub>20</sub> alkoxy carbonyl, aryl, C<sub>1</sub>-C<sub>20</sub> carboxylate,  
 9 C<sub>1</sub>-C<sub>20</sub> alkoxy, C<sub>2</sub>-C<sub>20</sub> alkenyloxy, C<sub>2</sub>-C<sub>20</sub> alkynylloxy, or  
 10 aryloxy, each R and R<sup>1</sup> optionally being substituted with  
 11 C<sub>1</sub>-C<sub>5</sub> alkyl, halogen, C<sub>1</sub>-C<sub>6</sub> alkoxy, or with a phenyl group  
 12 substituted with halogen, C<sub>1</sub>-C<sub>5</sub> alkyl or C<sub>1</sub>-C<sub>5</sub> alkoxy;  
 13 X and X<sup>1</sup> are independently selected from the group  
 14 consisting of anionic ligands; and  
 15 L and L<sup>1</sup> are selected from the group consisting of  
 16 nucleophilic carbenes, phosphine, sulfonated phosphine,  
 17 phosphite, phosphinite, phosphonite, ether, amine, amide,

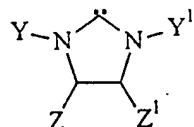
18 sulfoxide, carbonyl, nitrosyl, pyridine and thioether,  
19 wherein at least one of L or L<sup>1</sup> is a nucleophilic carbene.

1 10. The catalytic complex according to claim 9, wherein  
2 only one of L or L<sup>1</sup> is a nucleophilic carbene.

1 11. A catalytic complex according to claim 10, wherein  
2 one of L or L<sup>1</sup> is a phosphine.

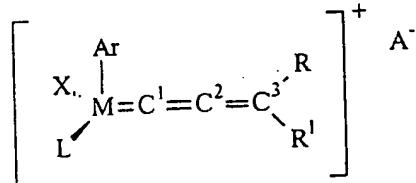
1 12. A catalytic complex according to claim 9, wherein at  
2 least 2 of X, X<sup>1</sup>, L or L<sup>1</sup> are bonded together to form a  
3 multidentate ligand.

1 13. A catalytic complex according to claim 9, wherein  
2 said nucleophilic carbene is of the formula:



3  
4 wherein  
5 Y and Y<sup>1</sup> are independently selected from the group  
6 consisting of hydrogen, C<sub>1</sub>-C<sub>20</sub> alkyl, C<sub>2</sub>-C<sub>20</sub> alkenyl, C<sub>2</sub>-C<sub>20</sub>  
7 alkynyl, C<sub>2</sub>-C<sub>20</sub> alkoxy carbonyl, aryl, C<sub>1</sub>-C<sub>20</sub> carboxylate,  
8 C<sub>1</sub>-C<sub>20</sub> alkoxy, C<sub>2</sub>-C<sub>20</sub> alkenyloxy, C<sub>2</sub>-C<sub>20</sub> alkynylloxy, or  
9 aryloxy, each Y and Y<sup>1</sup> optionally being substituted with  
10 C<sub>1</sub>-C<sub>5</sub> alkyl, halogen, C<sub>1</sub>-C<sub>6</sub> alkoxy, or with a phenyl group  
11 substituted with halogen, C<sub>1</sub>-C<sub>5</sub> alkyl or C<sub>1</sub>-C<sub>5</sub> alkoxy and;  
12 Z and Z<sup>1</sup> are independently selected from the group  
13 consisting of hydrogen, C<sub>1</sub>-C<sub>20</sub> alkyl, C<sub>2</sub>-C<sub>20</sub> alkenyl, C<sub>2</sub>-C<sub>20</sub>  
14 alkynyl, C<sub>2</sub>-C<sub>20</sub> alkoxy carbonyl, aryl, C<sub>1</sub>-C<sub>20</sub> carboxylate,  
15 C<sub>1</sub>-C<sub>20</sub> alkoxy, C<sub>2</sub>-C<sub>20</sub> alkenyloxy, C<sub>2</sub>-C<sub>20</sub> alkynylloxy, or  
16 aryloxy, each Z and Z<sup>1</sup> optionally being substituted with  
17 C<sub>1</sub>-C<sub>5</sub> alkyl, halogen, C<sub>1</sub>-C<sub>6</sub> alkoxy, or with a phenyl group  
18 substituted with halogen, C<sub>1</sub>-C<sub>5</sub> alkyl or C<sub>1</sub>-C<sub>5</sub> alkoxy,  
19 and wherein the ring can be optionally aromatic by  
20 introduction of a further double bond in the ring.

1 14. A catalytic complex of the formula:



2

3 wherein

4  $\text{C}^1$ ,  $\text{C}^2$  and  $\text{C}^3$  are  $\text{sp}^2$ -hybridized carbons, wherein  
5 either or both of  $\text{C}^1$  and  $\text{C}^2$  are optionally absent;  
6  $\text{M}$  is selected from the group consisting of Os and

7 Ru;

8  $\text{R}$  and  $\text{R}^1$  are independently selected from the group  
9 consisting of hydrogen,  $\text{C}_1\text{-C}_{20}$  alkyl,  $\text{C}_2\text{-C}_{20}$  alkenyl,  $\text{C}_2\text{-C}_{20}$   
10 alkynyl,  $\text{C}_2\text{-C}_{20}$  alkoxy carbonyl, aryl,  $\text{C}_1\text{-C}_{20}$  carboxylate,  
11  $\text{C}_1\text{-C}_{20}$  alkoxy,  $\text{C}_2\text{-C}_{20}$  alkenyloxy,  $\text{C}_2\text{-C}_{20}$  alkynyloxy, or  
12 aryloxy, each  $\text{R}$  and  $\text{R}^1$  optionally being substituted with  
13  $\text{C}_1\text{-C}_5$  alkyl, halogen,  $\text{C}_1\text{-C}_6$  alkoxy, or with a phenyl group  
14 substituted with halogen,  $\text{C}_1\text{-C}_5$  alkyl or  $\text{C}_1\text{-C}_5$  alkoxy;

15  $\text{X}$  is an anionic ligand; and

16  $\text{L}$  is a nucleophilic carbene; and

17  $\text{Ar}$  is an aryl substituent, bonded to  $\text{M}$  by an  $\eta^6$   
18 bond.

1 15. A catalytic complex according to claim 13, wherein

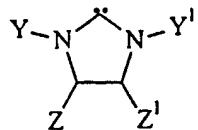
2 one of  $\text{L}$  or  $\text{L}^1$  is a phosphine.

1 16. A catalytic complex according to claim 13, wherein

2 at least 2 of  $\text{X}$ ,  $\text{X}^1$ ,  $\text{L}$  or  $\text{L}^1$  are bonded together to form a  
3 multidentate ligand.

1 17. A catalytic complex according to claim 13, wherein

2 said nucleophilic carbene is of the formula:



3

4 wherein

5       Y and Y<sup>1</sup> are independently selected from the group  
 6 consisting of hydrogen, C<sub>1</sub>-C<sub>20</sub> alkyl, C<sub>2</sub>-C<sub>20</sub> alkenyl, C<sub>2</sub>-C<sub>20</sub>  
 7 alkynyl, C<sub>2</sub>-C<sub>20</sub> alkoxy carbonyl, aryl, C<sub>1</sub>-C<sub>20</sub> carboxylate,  
 8 C<sub>1</sub>-C<sub>20</sub> alkoxy, C<sub>2</sub>-C<sub>20</sub> alkenyloxy, C<sub>2</sub>-C<sub>20</sub> alkynyloxy, or  
 9 aryloxy, each Y and Y<sup>1</sup> optionally being substituted with  
 10 C<sub>1</sub>-C<sub>5</sub> alkyl, halogen, C<sub>1</sub>-C<sub>6</sub> alkoxy, or with a phenyl group  
 11 substituted with halogen, C<sub>1</sub>-C<sub>5</sub> alkyl or C<sub>1</sub>-C<sub>5</sub> alkoxy and;

12       Z and Z<sup>1</sup> are independently selected from the group  
 13 consisting of hydrogen, C<sub>1</sub>-C<sub>20</sub> alkyl, C<sub>2</sub>-C<sub>20</sub> alkenyl, C<sub>2</sub>-C<sub>20</sub>  
 14 alkynyl, C<sub>2</sub>-C<sub>20</sub> alkoxy carbonyl, aryl, C<sub>1</sub>-C<sub>20</sub> carboxylate,  
 15 C<sub>1</sub>-C<sub>20</sub> alkoxy, C<sub>2</sub>-C<sub>20</sub> alkenyloxy, C<sub>2</sub>-C<sub>20</sub> alkynyloxy, or  
 16 aryloxy, each Z and Z<sup>1</sup> optionally being substituted with  
 17 C<sub>1</sub>-C<sub>5</sub> alkyl, halogen, C<sub>1</sub>-C<sub>6</sub> alkoxy, or with a phenyl group  
 18 substituted with halogen, C<sub>1</sub>-C<sub>5</sub> alkyl or C<sub>1</sub>-C<sub>5</sub> alkoxy,  
 19 and wherein the ring can be optionally aromatic by  
 20 introduction of a further double bond in the ring.

1       18. A method of making a nucleophilic carbene, said  
 2 method comprising:

3       a) contacting a substituted or unsubstituted  
 4 aniline with an approximately one-half equimolar amount  
 5 of paraformaldehyde under an inert atmosphere to make a  
 6 first reaction mixture;

7       b) heating said first reaction mixture until said  
 8 paraformaldehyde dissolves;

9       c) adding an approximately one-half equimolar  
 10 amount of a dialkoxyacetaldehyde to make a second  
 11 reaction mixture; and

12                   d) heating said second reaction mixture for a  
13                   time and under conditions sufficient to make a  
14                   nucleophilic carbene.

1       19. The method of claim 18, wherein said aniline is  
2       2,4,6-trimethylaniline.

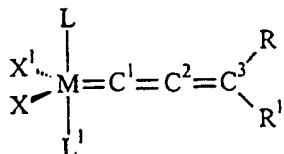
1       20. The method of claim 18, wherein said aniline is 2,6-  
2       diisopropylaniline.

1       21. The method of claim 18, further comprising the step  
2       of hydrogenating the nucleophilic carbene to produce a  
3       non-aromatic nucleophilic carbene.

1       22. A method of performing ring closing metathesis, said  
2       method comprising contacting a diterminal diene with a  
3       catalytic complex under conditions appropriate, and for a  
4       time sufficient to produce a cyclic alkene, wherein the  
5       catalytic complex comprises:

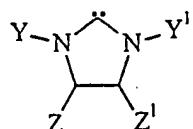
6                   a) a metal atom selected from the group  
7                   consisting of ruthenium or osmium;  
8                   b) at least one anionic ligand ligated to said  
9                   metal;  
10                  c) at least one nucleophilic carbene ligand  
11                  ligated to said metal;  
12                  d) a further ligand ligated to said metal; and  
13                  e) a carbon-containing ligand ligated to said  
14                  metal, wherein said carbon-containing ligand is  
15                  selected from the group consisting of  
16                  alkylidene, benzylidene, indenylidene, vinylidene,  
17                  and allenylidene.

1       23. The method of claim 22, wherein the catalytic  
2       complex has the formula:



3                   wherein M is Os or Ru;  
 4                   C<sup>1</sup>, C<sup>2</sup> and C<sup>3</sup> are sp<sup>2</sup>-hybridized carbons, wherein  
 5                   either or both of C<sup>1</sup> and C<sup>2</sup> are optionally absent;  
 6                   R and R<sup>1</sup> are independently selected from the group  
 7                   consisting of hydrogen, C<sub>1</sub>-C<sub>20</sub> alkyl, C<sub>2</sub>-C<sub>20</sub> alkenyl, C<sub>2</sub>-C<sub>20</sub>  
 8                   alkynyl, C<sub>2</sub>-C<sub>20</sub> alkoxy carbonyl, aryl, C<sub>1</sub>-C<sub>20</sub> carboxylate,  
 9                   C<sub>1</sub>-C<sub>20</sub> alkoxy, C<sub>2</sub>-C<sub>20</sub> alkenyloxy, C<sub>2</sub>-C<sub>20</sub> alkynyloxy, or  
 10                  aryloxy, each R and R<sup>1</sup> optionally being substituted with  
 11                  C<sub>1</sub>-C<sub>5</sub> alkyl, halogen, C<sub>1</sub>-C<sub>6</sub> alkoxy, or with a phenyl group  
 12                  substituted with halogen, C<sub>1</sub>-C<sub>5</sub> alkyl or C<sub>1</sub>-C<sub>5</sub> alkoxy;  
 13                  X and X<sup>1</sup> are independently selected from the group  
 14                  consisting of anionic ligands; and  
 15                  L and L<sup>1</sup> are selected from the group consisting of  
 16                  nucleophilic carbenes, phosphine, sulfonated phosphine,  
 17                  phosphite, phosphinite, phosphonite, ether, amine, amide,  
 18                  sulfoxide, carbonyl, nitrosyl, pyridine and thioether,  
 19                  wherein at least one of L or L<sup>1</sup> is a nucleophilic carbene.

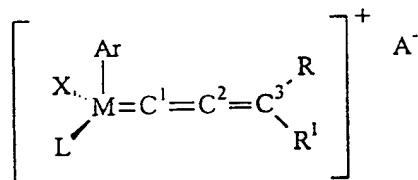
1 24. The method of claim 23, wherein the nucleophilic  
2 carbene has the formula:



3  
4 wherein  
5       Y and Y<sup>1</sup> are independently selected from the group  
6 consisting of hydrogen, C<sub>1</sub>-C<sub>20</sub> alkyl, C<sub>2</sub>-C<sub>20</sub> alkenyl, C<sub>2</sub>-C<sub>20</sub>  
7 alkynyl, C<sub>2</sub>-C<sub>20</sub> alkoxy carbonyl, aryl, C<sub>1</sub>-C<sub>20</sub> carboxylate,  
8 C<sub>1</sub>-C<sub>20</sub> alkoxy, C<sub>2</sub>-C<sub>20</sub> alkenyloxy, C<sub>2</sub>-C<sub>20</sub> alkynylloxy, or  
9 aryloxy, each Y and Y<sup>1</sup> optionally being substituted with

10  $C_1-C_5$  alkyl, halogen,  $C_1-C_6$  alkoxy, or with a phenyl group  
 11 substituted with halogen,  $C_1-C_5$  alkyl or  $C_1-C_5$  alkoxy and;  
 12        $Z$  and  $Z^1$  are independently selected from the group  
 13 consisting of hydrogen,  $C_1-C_{20}$  alkyl,  $C_2-C_{20}$  alkenyl,  $C_2-C_{20}$   
 14 alkynyl,  $C_2-C_{20}$  alkoxy carbonyl, aryl,  $C_1-C_{20}$  carboxylate,  
 15  $C_1-C_{20}$  alkoxy,  $C_2-C_{20}$  alkenyloxy,  $C_2-C_{20}$  alkynylloxy, or  
 16 aryloxy, each  $Z$  and  $Z^1$  optionally being substituted with  
 17  $C_1-C_5$  alkyl, halogen,  $C_1-C_6$  alkoxy, or with a phenyl group  
 18 substituted with halogen,  $C_1-C_5$  alkyl or  $C_1-C_5$  alkoxy,  
 19 and wherein the ring can be optionally aromatic by  
 20 introduction of a further double bond in the ring.

1 25. The method of claim 22, wherein the catalytic  
 2 complex has the formula:



3

4

5

6 wherein

7        $C^1$ ,  $C^2$  and  $C^3$  are  $sp^2$ -hybridized carbons, wherein  
 8 either or both of  $C^1$  and  $C^2$  are optionally absent;  
 9       M is selected from the group consisting of Os and  
 10 Ru;

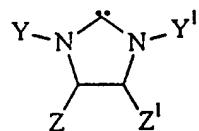
11       R and  $R^1$  are independently selected from the group  
 12 consisting of hydrogen,  $C_1-C_{20}$  alkyl,  $C_2-C_{20}$  alkenyl,  $C_2-C_{20}$   
 13 alkynyl,  $C_2-C_{20}$  alkoxy carbonyl, aryl,  $C_1-C_{20}$  carboxylate,  
 14  $C_1-C_{20}$  alkoxy,  $C_2-C_{20}$  alkenyloxy,  $C_2-C_{20}$  alkynylloxy, or  
 15 aryloxy, each R and  $R^1$  optionally being substituted with  
 16  $C_1-C_5$  alkyl, halogen,  $C_1-C_6$  alkoxy, or with a phenyl group  
 17 substituted with halogen,  $C_1-C_5$  alkyl or  $C_1-C_5$  alkoxy;

18       X is an anionic ligand; and

19       L is a nucleophilic carbene; and

20                   Ar is an aryl substituent, bonded to M by an  $\eta^6$   
21                   bond.

1   26. The method of claim 25, wherein the nucleophilic  
2   carbene has the formula:



3  
4                   wherein  
5                   Y and Y' are independently selected from the group  
6                   consisting of hydrogen, C<sub>1</sub>-C<sub>20</sub> alkyl, C<sub>2</sub>-C<sub>20</sub> alkenyl, C<sub>2</sub>-C<sub>20</sub>  
7                   alkynyl, C<sub>2</sub>-C<sub>20</sub> alkoxy carbonyl, aryl, C<sub>1</sub>-C<sub>20</sub> carboxylate,  
8                   C<sub>1</sub>-C<sub>20</sub> alkoxy, C<sub>2</sub>-C<sub>20</sub> alkenyloxy, C<sub>2</sub>-C<sub>20</sub> alkynyloxy, or  
9                   aryloxy, each Y and Y' optionally being substituted with  
10                   C<sub>1</sub>-C<sub>5</sub> alkyl, halogen, C<sub>1</sub>-C<sub>6</sub> alkoxy, or with a phenyl group  
11                   substituted with halogen, C<sub>1</sub>-C<sub>5</sub> alkyl or C<sub>1</sub>-C<sub>5</sub> alkoxy and;  
12                   Z and Z' are independently selected from the group  
13                   consisting of hydrogen, C<sub>1</sub>-C<sub>20</sub> alkyl, C<sub>2</sub>-C<sub>20</sub> alkenyl, C<sub>2</sub>-C<sub>20</sub>  
14                   alkynyl, C<sub>2</sub>-C<sub>20</sub> alkoxy carbonyl, aryl, C<sub>1</sub>-C<sub>20</sub> carboxylate,  
15                   C<sub>1</sub>-C<sub>20</sub> alkoxy, C<sub>2</sub>-C<sub>20</sub> alkenyloxy, C<sub>2</sub>-C<sub>20</sub> alkynyloxy, or  
16                   aryloxy, each Z and Z' optionally being substituted with  
17                   C<sub>1</sub>-C<sub>5</sub> alkyl, halogen, C<sub>1</sub>-C<sub>6</sub> alkoxy, or with a phenyl group  
18                   substituted with halogen, C<sub>1</sub>-C<sub>5</sub> alkyl or C<sub>1</sub>-C<sub>5</sub> alkoxy,  
19                   and wherein the ring can be optionally aromatic by  
20                   introduction of a further double bond in the ring.

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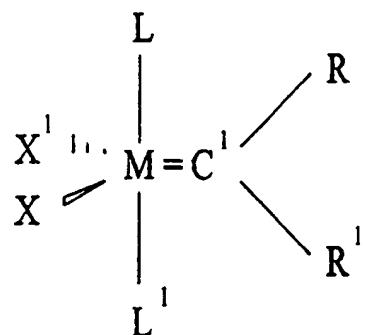


FIG. 1A

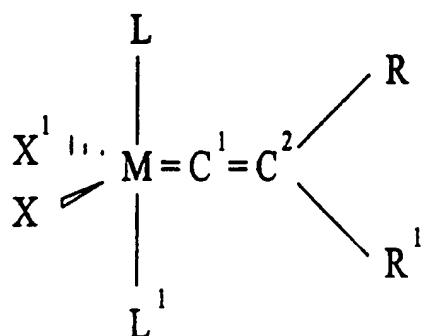


FIG. 1B

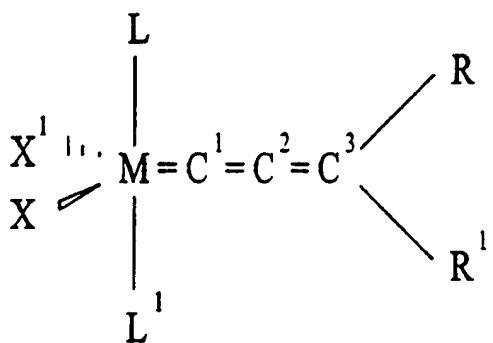


FIG. 1C

SUBSTITUTE SHEET (RULE 26)

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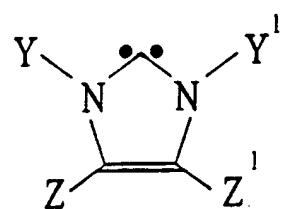


FIG. 2A

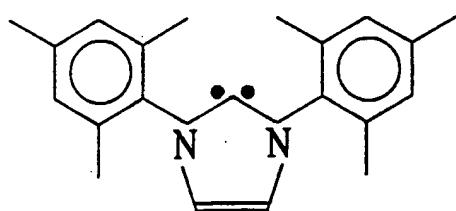


FIG. 2B

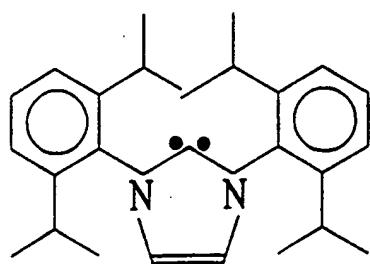


FIG. 2C

SUBSTITUTE SHEET (RULE 26)

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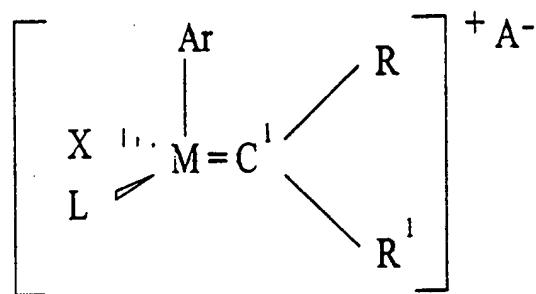


FIG. 3A

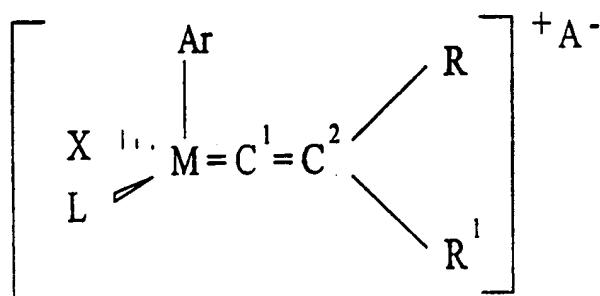


FIG. 3B

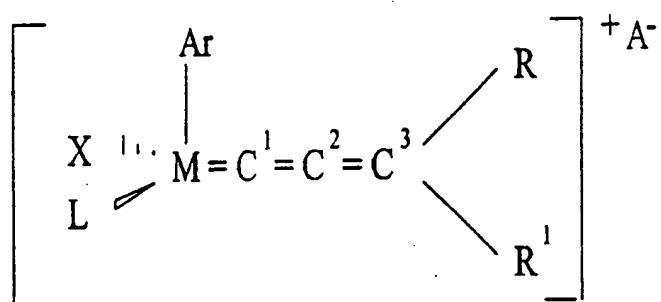


FIG. 3C

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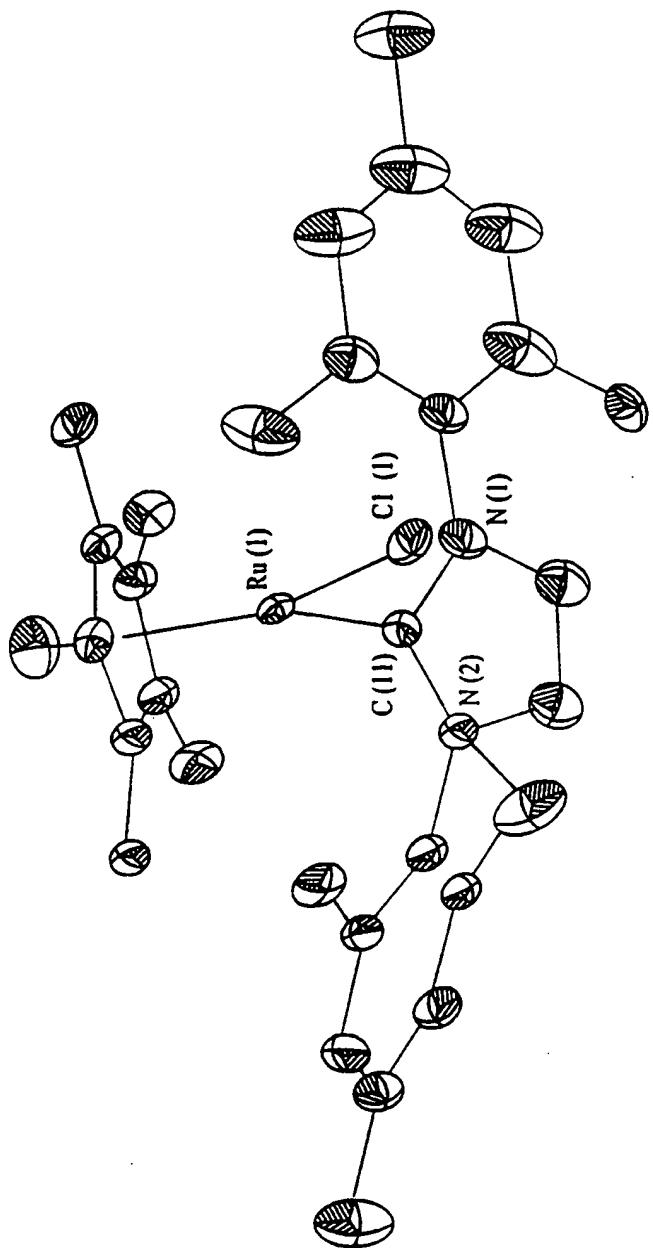


FIG. 4

## **SUBSTITUTE SHEET (RULE26)**

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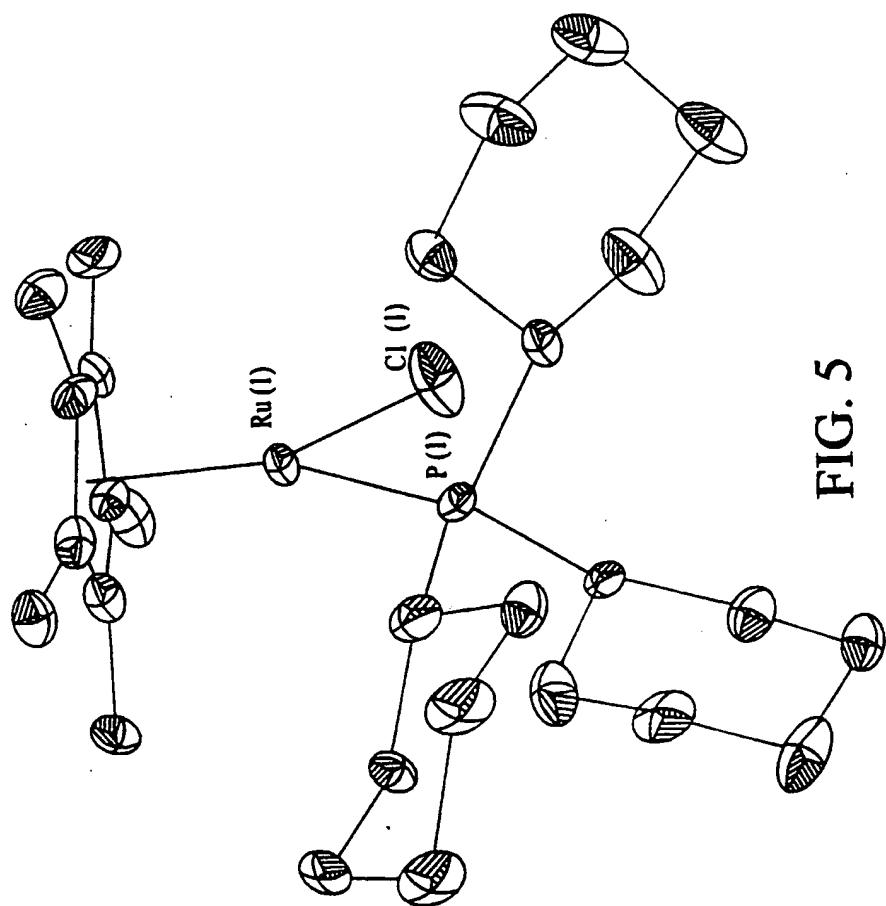


FIG. 5

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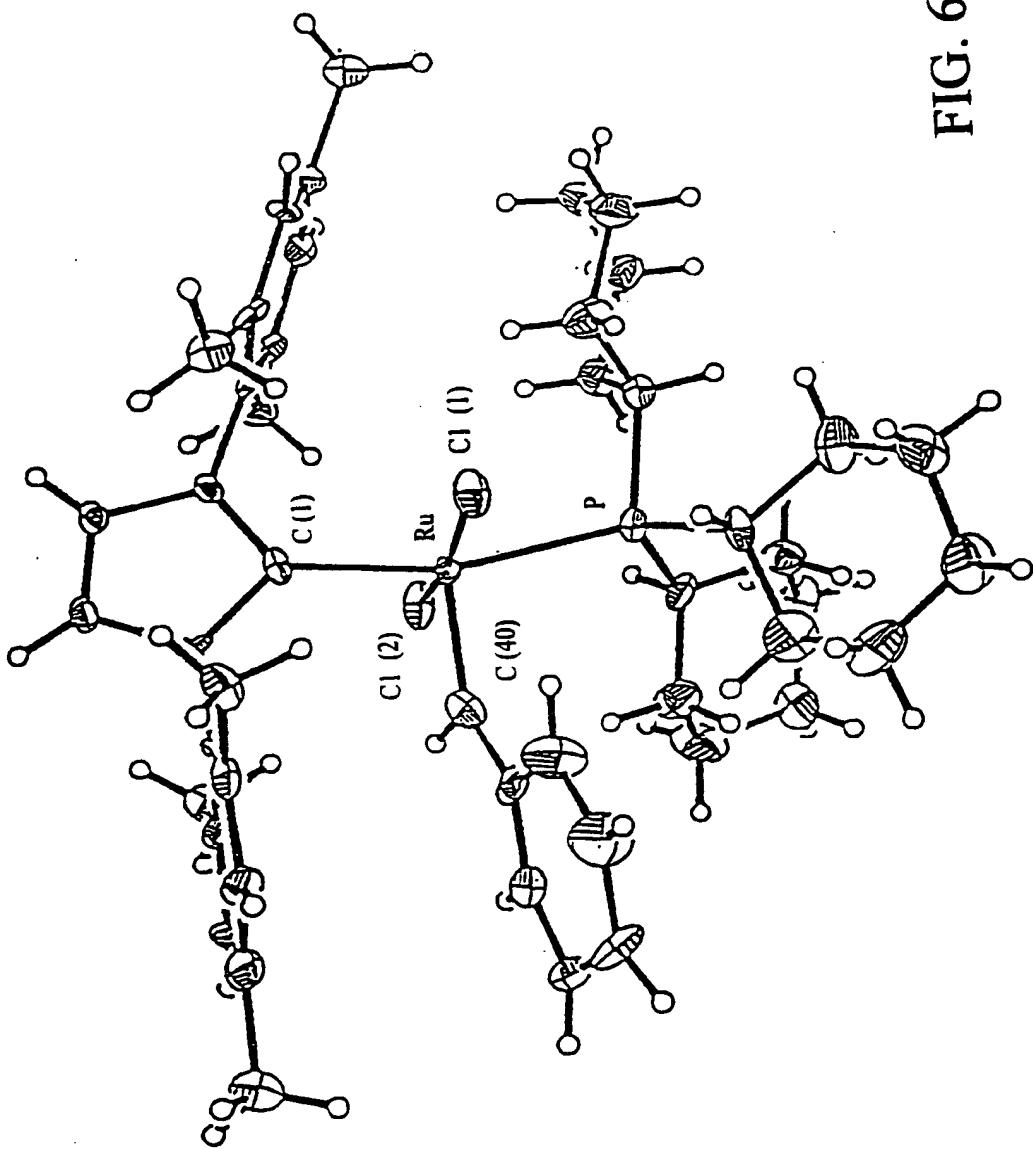


FIG. 6

## INTERNATIONAL SEARCH REPORT

International application No.

PCT/US99/20629

## A. CLASSIFICATION OF SUBJECT MATTER

IPC(6) :B01J 31/00; C07F 9/02, 15/00; C07C 13/00  
 US CL :502/152, 162; 548/103; 556/21, 136, 137; 560/508; 585/350

According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

U.S. : 502/152, 162; 548/103; 556/21, 136, 137; 560/508; 585/350

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

REGISTRY and CA Databases

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	WO 96/04289 A1 (CALIFORNIA INSTITUTE OF TECHNOLOGY) 15 February 1996, see entire document.	1-26
A	IVIN, KENNETH J., Some recent applications of olefin metathesis in organic synthesis: A review. Journal of Molecular Catalysis A: Chemical. 1998, Vol. 133, No. 1-2, pages 1-16, see entire document.	1-26

Further documents are listed in the continuation of Box C.  See patent family annex.

Special categories of cited documents:	"T"	later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
"A" document defining the general state of the art which is not considered to be of particular relevance		
"B" earlier document published on or after the international filing date	"X"	document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)	"Y"	document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
"O" document referring to an oral disclosure, use, exhibition or other means	"A"	document member of the same patent family
"P" document published prior to the international filing date but later than the priority date claimed		

Date of the actual completion of the international search	Date of mailing of the international search report
16 NOVEMBER 1999	23 DEC 1999

Name and mailing address of the ISA/US Commissioner of Patents and Trademarks Box PCT Washington, D.C. 20231 Facsimile No. (703) 305-3230	Authorized officer <i>Fortino Nazario-Gonzalez</i> Telephone No. (703) 308-1235
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